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THE NATURE OF THE HIGHER SILVER OXIDE

A. B. Neyding, I. A. Kazarnovskiy

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THE NATURE OF THE HIGHER SILVER OXIDE

A. B. Neyding and USSR Academy of Sciences Associate Member,
I. A. Kazarnovskiy

ABSTRACT

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The magnetic susceptibility of certain physico-chemical properties of the AgO oxide is studied. It is found that this oxide is diamagnetic, and that the anomaly of the AgO magnetic properties is caused by specific features of the crystalline lattice of this oxide.

author

The existence of two silver oxides: Ag_2O and AgO has definitely /713* been established at the present time. The Ag_2O oxide, which has been studied to the greatest extent, has a crystalline structure of the cuprite type (Ref. 1). The bonds in this brown substance evidently deviate significantly from the ion type (Ref. 2). With respect to the higher silver oxide** which was described long ago, in spite of a great deal of research, its nature is still not clear. Several authors have regarded this oxide as a compound or bivalent silver, similar to CuO (Ref. 3, 4). Other authors have regarded it as Ag_2O_2 peroxide with monovalent silver, similar to Na_2O_2 (Ref. 5,6). AgO is a fine crystalline powder which is grayish-black in color. It has not been possible to determine the crystalline structure of this oxide up to the present.

* Note: Numbers in the margin indicate pagination in the original foreign text.

** See, for example, (Ref. 3-5).

The position of silver in the D. I. Mendeleev periodic system does not exclude the possibility that bi- and tri-valent silver may also exist, along with monovalent silver. The excited state of a silver atom, caused by the $d^{10}s \rightarrow d^9sp$ conversion, corresponds to a higher degree of valence.

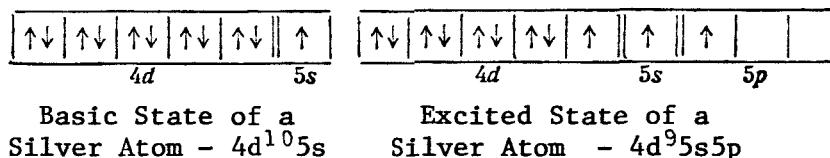
Theory requires the following magnetic properties for different valent states of silver: Irrespective of whether the bond is an ion or covalent bond, monovalent silver must be diamagnetic, and bivalent silver must be paramagnetic with one unconnected electron. Trivalent silver is diamagnetic when there are covalent bonds, and may be paramagnetic when an Ag^{+++} ion is formed which has an electron structure d^8 with two unconnected electrons, according to the law of maximal multiplicity.

Experiments established the diamagnetism of such monovalent silver compounds as Ag_2O (Ref. 6), $AgCl$, $AgBr$ and others (Ref. 7). Paramagnetism corresponding to one unconnected electron (Ref. 8, 9) was found in several complex bivalent silver compounds (for example, $Ag(ClO_3)_2 \cdot 2 \text{ Dipyr.}$; $Ag_2S_2O_8 \cdot 4 \text{ Pyr.}$, etc.). The application of the magnetic criterion to AgO has not as yet provided a definitive answer to the question of the valence of silver in this oxide (Ref. 7, 9).

We made a new study of the magnetic susceptibility of certain physico-chemical properties of AgO oxide.

Pure preparations with a content of 99.4-99.8% AgO were obtained by /714 anode oxidation of a 10% silver nitrate solution with the subsequent use of boiling water to decompose the dark crystals of the Ag_7NO_{11} nitrate group formed at the anode (Ref. 5).

Several chemical properties of AgO were studied. As a careful study has shown, hydrogen peroxide is not separated out when dilute acids (H_2SO_4 , $HClO_4$)



act upon AgO. With concentrated nitric acid, AgO forms a dark brown solution, without giving off oxygen (Ref. 3). When diluted with water or when heated, the brown solution becomes discolored and gives off oxygen. AgO is a strong oxidizer: At room temperature, SO₂ is oxidized into SO₃, and ammonia (gaseous and in an aqueous solution) - into nitrogen, nitrates, and nitrites

Measurements of the AgO density led to a value of $d_4^{25} = 7.485 \pm 0.004$, in accordance with data given in the literature (Ref. 10). This provides a molecular volume of 16.55 cm³.

The electroconductivity of AgO, in the form of small cylinders made of a powder pressed under a pressure of up to 12,000 kg/cm²*, was measured by the compensation method at temperatures ranging between +20 and -40°. Measurements performed on seven samples led to a mean specific electroconductivity of $\sigma_{20} = 7 \cdot 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} \pm 15\%^{**}$. A positive temperature conductivity coefficient was discovered (see Figure 1), which indicates that AgO belongs to electron semiconductors. The electron nature of its conductivity, as well as its relatively high value, indicates the presence of mobile electrons in the crystalline lattice of AgO.

Measurements of AgO magnetic susceptibility, performed according to the

* The small cylinders have a metallic luster.

** The tentative measurements of Le Blanc and Sacchse (Ref. 11), which were conducted at 20°, provided a value of $\sigma_{20} = 1 \cdot 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$.

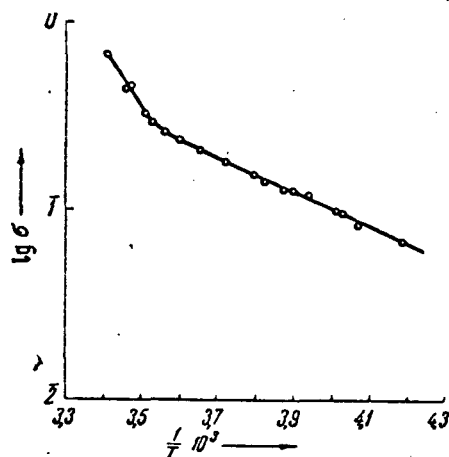


Figure 1

Temperature Dependence of AgO Electroconductivity for
a Sample Pressed Under a Pressure of 10,000 kg/cm²

Gouy method at temperatures ranging between +95 and -183°, indicated the diamagnetism of this oxide. The results obtained are presented in Table 1.

The value $\chi_g = -0.155 \cdot 10^{-6}$ obtained at room temperature gives $\chi_M = 19.1 \cdot 10^{-6}$ per mole.

The magnetic susceptibility of the Ag₇NO₁₁ nitrate group was also determined, to which the formula 2Ag₂O₃·2AgO·AgNO₃ is attributed (Ref. 3, 5), as well as the silver ion in the brown solution already mentioned, which was obtained by the action of concentrated nitric acid on AgO. The nitrate group was paramagnetic; its molar susceptibility at 17° was $\chi_M = +780 \cdot 10^{-6}$ *. The susceptibility of the silver ion in the brown solution - with conversion to Ag(NO₃)₂ - was determined by the difference in the diamagnetism of the original products and of the solution, and was calculated according to the formula:

$$\chi_g = \frac{100\chi_1 - (100 - p)\chi_2}{p},$$

* The X-ray structure of this substance was studied by Z. V. Zvonkova and G. S. Zhdanov (Ref. 12).

TABLE 1
MAGNETIC SUSCEPTIBILITY OF AgO

Preparation No.	AgO Content in %	95°		14°		-78°		-183°	
		$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$
1	99,4	—	—	-0,153	-18,9	—	—	—	—
2	99,8	—	—	-0,158	-19,6	-0,121	-15,0	-0,022	-2,7
3	99,6	-0,198	-24,5	-0,155	-19,1	-0,101	-12,4	-0,028	-3,5

where χ_g is the gram susceptibility of $\text{Ag}(\text{NO}_3)_2$, χ_1 - susceptibility of one gram of brown solution, χ_2 - susceptibility of 1 g of solvent, and p - percentage content of $\text{Ag}(\text{NO}_3)_2$ in the brown solution.

The results obtained are presented in Table 2.

TABLE 2

Experi- ment No.	$\text{Ag}(\text{NO}_3)_2$ Con- tent in %	t°	$\chi_2 \cdot 10^6$	$\chi_1 \cdot 10^6$	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	Effective Magnetic Moment of an Ag^{++} Ion, μ_{eff} Bohr Magnetron
1	3,58	15,1	-0,496	-0,282	+5,48	+1350	1,76
2	2,75	13,2	-0,467	-0,300	+5,61	+1380	1,77
Mean Value . . .					+5,55	+1365	1,76

* Corrected for the diamagnetism of NO_3^- ions utilizing the value $\chi_{\text{NO}_3^-} = -21 \cdot 10^{-6}$.

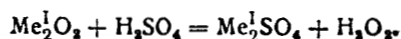
The value found for the magnetic moment of 1.76 Bohr magnetons is normal for an ion of bivalent silver Ag^{++} with one unconnected electron.

The experimental data obtained throw new light on the nature of the AgO oxide. When acids act upon AgO, oxygen is given off, and not hydrogen peroxide.

Consequently, AgO is not a true peroxide according to the criterion of D. I. Mendeleev (Ref. 13). Under the influence of acids, the liberation of oxygen apparently follows the reaction



in contrast to peroxides which react according to the equation



Thus, the oxidizing ability of AgO, in contrast to the peroxides, is caused by a change in the metal valence during the reaction process.

A comparison between the volumetric relationships of silver oxides and the oxides of alkali and alkali-earth metals reveals a characteristic difference. When peroxides are formed from oxides, the increase in the molecular volume is 4-6 cm³. Thus, for example, $\text{MV}_{\text{Na}_2\text{O}_2} - \text{MV}_{\text{Na}_2\text{O}} = 31.3$ (Ref. 14) - 25.9 (Ref. 15) = 5.4 cm³. When there is a conversion from a lower silver oxide to a higher silver oxide, the corresponding increase is only $2\text{MV}_{\text{AgO}} = \text{MV}_{\text{Ag}_2\text{O}} = 2 \cdot 16.55 - 32.1$ (Ref. 10) = 1.0 cm³ in all*. In the latter case, the volume changes very little, since the increase in the metal valence leads to a decrease in the intratomic distances in the crystalline lattice, which almost compensates for the volumetric increase which diminishes per each unnecessary oxygen atom.

The results derived from magnetic measurements of AgO lead to an apparent contradiction, since the magnetic moment of this oxide equals zero, instead of the value of 1.73 Bohr magnetons which is normal for bivalent silver. However, the paramagnetism of silver which was discovered in the brown solution shows that a change in the surroundings of silver atoms in AgO - i.e., a change from a lattice to a solution - leads to a magnetic moment which is normal for

* The increase in the molecular volume is 0.8 cm³ for copper oxides.

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